

High-Level *Ab Initio* Versus DFT Calculations on $(\text{H}_2\text{O}_2)_2$ and $\text{H}_2\text{O}_2\text{--H}_2\text{O}$ Complexes As Prototypes of Multiple Hydrogen Bond Systems

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ABSTRACT: The performance of B-LYP, B-P86, B3-LYP, B3-P86, and B3-PW91 density functionals to describe multiple hydrogen bond systems was studied. For this purpose we have chosen the dimers of hydrogen peroxide and the hydrogen peroxide–water complexes. The geometries and vibrational frequencies obtained with a 6-311 + G(d, p) basis set were compared with those obtained at the MP2 level using the same basis set expansion. The corresponding dimerization energies were obtained using a 6-311 + G(3df, 2p) basis set and compared with those obtained using the G2(MP2) theory. Red shiftings of the OH donor stretching frequencies were predicted by all approaches investigated; however, in all cases, the DFT values were sizably larger than the MP2 ones. Similarly, the blue shifting of the torsion of the hydrogen peroxide subunit was larger when evaluated at the DFT level. All functionals reproduced the G2(MP2) relative stabilities of the different local minima quite well. With the exception of the B-LYP and B3-PW91 approaches, all functionals yielded binding energies which deviated from the G2(MP2) values by less than 0.5 kcal/mol, provided that G2-type basis sets were used and that the corresponding BSSE corrections were included. © 1997 by John Wiley & Sons, Inc. *J Comput Chem* **18**: 1124–1135, 1997

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Introduction

The role of hydrogen bonds (HB) in the structure and stability of molecular and biomolecular complexes is very important because many chemical, physical, and biological processes involve the formation and/or breaking of this kind of bonds.¹ A particularly interesting case is that of hydrogen peroxide.^{2–5} Hydrogen peroxide is a byproduct of several metabolic reactions including the conversion of hypoxanthine to xanthine.⁶ It is also involved in the “respiratory burst” following neutrophil phagocytosis,⁷ and recent findings suggest that any biological effects of H_2O_2 in aqueous solution are actually mediated by hydrogen bonded complexes of H_2O_2 and other compounds found in biochemical systems. On the other hand, hydrogen peroxide and its complexes provide suitable benchmark systems for studying much weaker interactions than typical chemical bonds and require, therefore, calculations with high accuracy. It is well known that electron correlation has to be included when studying the structure and properties of hydrogen bonded systems. Furthermore, very flexible basis sets including diffuse components are needed. Hence, most high quality theoretical studies concentrate on HB dimers of small molecules,⁸ because calculations with flexible basis sets and including electron correlation effects are computationally very expensive. A cheaper alternative is based on the use of density functional theory (DFT) that contains an inexpensive but rigorous approach to electron correlation. Thus, it can be applied to fairly large molecular systems even if large basis sets are required, because the need for computational resources in DFT formally scales as n^3 , where n is the number of basis functions, instead of at least n^5 for the MP2 method. In this article we aim at testing the validity of different DFT approaches to correctly describe hydrogen bonded complexes. Some studies in the same sense have been recently reported in the literature,^{9–20} but most deal with dimers in which a single HB is formed. In the present work we have chosen, as suitable examples, the hydrogen peroxide dimers and the hydrogen peroxide–water complexes, where each moiety may behave either as a hydrogen bond donor or as hydrogen bond acceptor, yielding cyclic structures that involve two hydrogen bonds, which are not always identical. For the aforementioned systems, the ge-

ometries, harmonic vibrational frequencies, zero point energies, and dimerization energies obtained in the framework of the DFT theory will be compared with those obtained using high-level *ab initio* techniques.^{4,5}

Computational Details

All calculations described in this work were performed using the GAUSSIAN 94 package of programs.²¹ The functionals used are separated into exchange and correlation parts. Local exchange-correlation functionals were not used because they have been shown to give a poor description of the properties of complexes which present intra- or intermolecular hydrogen bonds.^{10,14,17,20} The nonlocal exchange functional of Becke (B),²² including a gradient correction, was used with the gradient corrected functional of Lee, Yang, and Parr (LYP)²³ and the P86 functional corresponding to the gradient correction of Perdew together with its local functional.^{24–26} A hybrid method proposed by Becke, which includes a mixture of Hartree–Fock exchange with DFT correlation, was also employed. This functional, described as Becke3 (B3),^{27,28} is the three-parameter exchange functional containing the Slater exchange functional,²⁹ Hartree–Fock, and Becke’s 1988 gradient correction.³⁰ We combined this nonlocal hybrid functional with three different correlation functionals: the aforementioned LYP and P86, and the PW91 functional which is the Perdew and Wang gradient-corrected functional.³¹ In the X—C notation proposed recently by Pople and coworkers,³² where X is the name of the exchange functional combined with the correlation functional C, the combinations tested in this work can be summarized as B-LYP, B-P86, B3-LYP, B3-P86, and B3-PW91. The exact exchange and Coulomb integrals are evaluated analytically, whereas the integrals over the exchange and correlation functionals are done numerically. A grid, which has about 7000 points per atom, was used to reduce errors arising from this numerical integration.

Two different basis sets have been used in the optimization of the equilibrium geometries of the $(\text{H}_2\text{O}_2)_2$ and $(\text{H}_2\text{O}_2\text{--H}_2\text{O})$ systems, namely 6-31 + G(d,p) and 6-311 + G(d,p). The 6-31 + G(d,p) basis set was chosen because it was found to be the minimum basis set providing reasonable hydrogen bonded structures.¹⁹ The second one was considered in order to check whether an improve-

ment in the description of the valence shell has sizeable effects on the optimized geometries. This was the basis set employed in the MP2 geometry optimizations reported in the literature.^{4,5} Analytical harmonic vibrational frequencies were calculated for the monomers and dimers at the same optimization level of theory to confirm they are equilibrium points of the potential energy surface and to evaluate zero-point vibrational energies (ZPE). The DFT/6-311 + G(d,p)-optimized structures were then used for single point calculations using 6-311 + + G(3df,2p) and 6-311 + G(3df,2p) basis sets, respectively.

The binding energies were calculated as the difference between the dimer energy and the energy of the isolated monomers. The ZPE corrections are quite significant in hydrogen bonded systems where they may account for as much as the 50% of the total stabilization energy. Therefore, the dimerization energy will systematically include the ZPE correction. As recently shown by Bauschlicher,³³ scaling factors for B-LYP, B-P86, B3-LYP, and B3-P86 are very close to unity. Hence, neither DFT frequencies nor ZPE corrections were scaled.

The dimerization energies are also affected by the basis set superposition error (BSSE). This effect is particularly noticeable when dealing with binding energies of 5 kcal/mol or less, because even a BSSE estimation of 0.5 kcal/mol represents a high percentage of the binding energy. As shown in the literature,^{2,3,34} BSSE could be neglected using a very large basis set at the HF level, but when correlated calculations are performed, BSSE may be still very large, even if diffuse functions are included in the basis. There exists some controversy regarding the proper way to account for the BSSE. The approach most widely used to correct for BSSE is the full counterpoise method (FCP) of Boys and Bernardi³⁵:

$$\text{BSSE}(A - B) = E(A)_A - E(A)_{AB} \\ + E(B)_B - E(B)_{AB}$$

where $E(A)_{AB}$ and $E(B)_{AB}$ represent the energies of monomers A and B evaluated using their geometries within the dimer and the complete set of basis functions used to described the dimer, whereas $E(A)_A$ and $E(B)_B$ are the energies of the same molecules, but using only the basis functions centered on each monomer. This procedure has been criticized for both overestimating and underestimating the actual BSSE.^{36,37} However, Feller's calculations³⁴ on the water dimer showed good

agreement for those energies FCP corrected with the basis set limit interaction energies. Similar trends were observed previously by Szczesniak et al.³⁸ Therefore, we have evaluated the BSSE using the FCP method with the 6-311 + G(3df,2p) and 6-311 + + G(3df,2p) basis sets at the DFT level.

The DFT dimerization energies will be compared with those calculated at three different *ab initio* levels, namely, MP2/6-311 + G(3df,2p)//MP2/6-311 + G(d,p), MP2/6-311 + + G(3df,2p)//MP2/6-311 + G(d,p), and G2(MP2). In this respect, it should be noted that, although in the standard G2(MP2) procedure both the QCISD(T)/6-311G(d,p) and the MP2/6-311 + G(3df,2p) single point calculations are carried out on MP2/6-31G*-optimized geometries, in our case the MP2/6-311 + G(d,p)-optimized structures reported in Mó et al.^{4,5} were used. For consistency, the ZPE corrections were evaluated at the same level and scaled by the empirical factor 0.93. Likewise, the BSSE at the G2(MP2) level was quantified by computing the QCISD(T)/6-311G(d,p), MP2/6-311 + G(3df,2p), and MP2/6-311G(d,p) contributions on MP2/6-311 + G(d,p)-optimized structures.

Results and Discussion

Water, **1**, or hydrogen peroxide, **2**, molecules can behave in different ways—as single HB donors (d), as single HB acceptors (a), as HB bidonor (dd), and as HB biacceptor (aa). Accordingly, different complexes can be envisaged for the hydrogen peroxide dimer as well as for the hydrogen peroxide–water complex. Previous results showed that both potential energy surfaces of hydrogen peroxide dimers⁴ and hydrogen peroxide–water complexes⁵ present two minima, which have been schematized in Figure 1. In the hydrogen peroxide dimers, these minima (**3**, **4** in Fig. 1) correspond to a/d/a/d and a/d/ad/0 sequences, respectively. This implies that, in the global minimum, **3**, both oxygen atoms of each monomer participate in the bonding, one as HB donor and the other as HB acceptor. In the second minimum, **4**, only one monomer involves their two oxygen atoms in the hydrogen bonding, whereas the other monomer participates with only one of its oxygen atoms, which behaves simultaneously as HB donor and as HB acceptor. Their total energies are given as Supplementary Material.

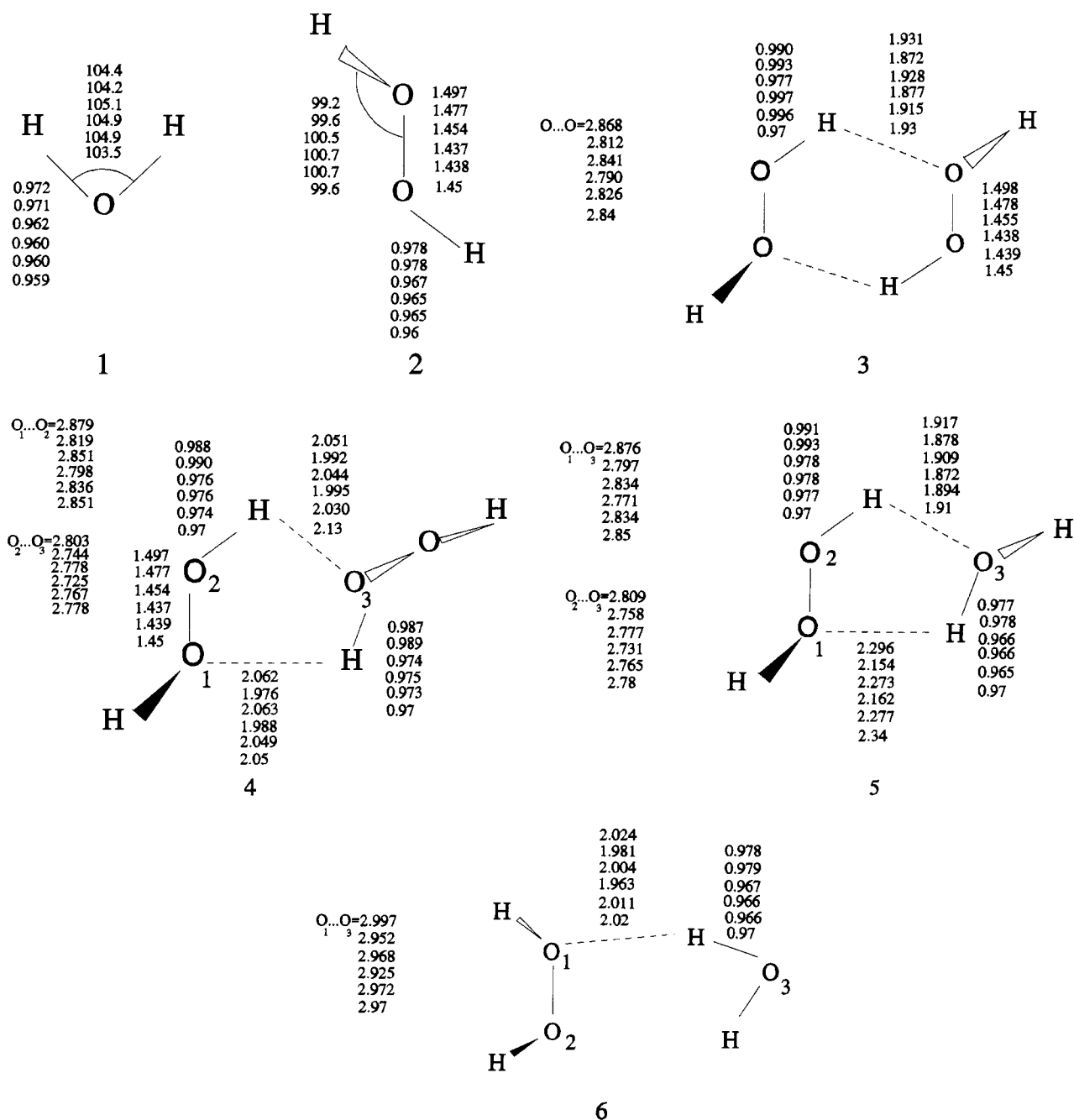


FIGURE 1. Optimized geometries for water (1), hydrogen peroxide (2), hydrogen peroxide dimers (3 and 4), and hydrogen peroxide–water complexes (5 and 6). Interatomic distances are given in angstroms and bond angles in degrees. The values for each geometrical parameter are given in the following order: B-LYP, B-P86, B3-LYP, B3-P86, B3-PW91, and MP2. In all cases, the optimizations were carried out at the 6-311 + G(d, p) level.

GEOMETRIES

The differences between the DFT geometrical parameters optimized at the 6-31 + G(d,p) and at the 6-311 + G(d,p) levels were found to be negligible with all the functionals used. This means that the equilibrium structures of these hydrogen bonded complexes are not very sensitive to the improving of the description of the outer valence region of the oxygen atoms. Therefore, for the sake of conciseness, we present in Figure 1 only the results obtained with the most flexible basis set. Only the most relevant parameters to characterize the hydrogen bonding, the $O \cdots O$, $O \cdots H$, and the $O-H_b$ distances, are given in the figure. In what follows, we will designate, as H_a , the hydrogen atoms not involved in the HB and, as H_b , the ones that participate in the hydrogen bonding between both monomers.

For water and hydrogen peroxide monomers and all complexes, all hybrid functionals yield geometries in fairly good agreement with the MP2 ones. There are, however, some exceptions that deserve mention. The B-LYP functional overestimates the $O-O$ distance of hydrogen peroxide either in the isolated molecule or when it forms part of the different dimers we are dealing with. A similar effect, although smaller, is found for the B-P86 functional. The B-LYP functional also overestimates the $O \cdots O$ distances concerned, whereas the B-P86 and the B3-P86 approaches yield $O \cdots O$ distances shorter than the MP2-optimized values. The remaining functionals yield $O \cdots O$ distances consistently close to the MP2 ones, although slightly smaller. A similar finding was reported for water dimers and water trimers.³⁹ Unfortunately, and to the best of our knowledge, for hydrogen peroxide dimers no experimental values have been reported for comparison. It is worth noting that, for water dimers and water trimers, either the DFT or the MP2 values are slightly too short with respect to the experimental ones, so for dimers involving hydrogen peroxide this probably will be also the case. Also, similar to what was found for water dimer and water trimers, all functionals give slightly shorter $O \cdots H$ distances than the MP2 method. This effect is particularly large when the B-P86 and the B3-P86 approaches are used, whereas the B-LYP values are, in some instances, slightly greater than the MP2 ones.

The most significant disagreement between MP2 and DFT values involves the $O1 \cdots H$ and the

$O3 \cdots H$ distances in dimer 4. At the MP2 level, the former is predicted to be smaller than the latter, whereas, at the DFT level, with the exception of the B-P86 and B3-P86 functionals, the opposite is found. It must be also noted that the B-LYP and B-P86 functionals yield also $O-H$ bond lengths systematically greater than the remaining functionals investigated. However, no matter which approach is used, the $O-H_b$ bond lengths are predicted to increase by about 0.010 to 0.012 Å upon dimerization.

A comparison of the individual geometrical parameters, bond lengths and bond angles, is not always the best procedure to establish the similarity between two optimized geometries. A more reliable way would be to compare the corresponding rotational constants. From Table I it is evident that the B-LYP and B-P86 rotational constants deviate significantly (about 7%) from those obtained with the other functionals, whose rotational constants differ among each other by an average of about 2%. It can be also seen that, in general, these DFT values are not far from the MP2 ones. Dimer 6 is an exception to this general behavior and the differences between MP2 and DFT rotational constants are about ten times higher than for the remaining dimers. This is so because in this case the relative orientation of the H_2O subunit with respect to the H_2O_2 moiety is slightly different for MP2 than for DFT-optimized geometries. Whereas the MP2 $O \cdots O$ distance between the two oxygen atoms that do not participate in the HB is 3.1 Å, the DFT values (about 3.6 Å) are much larger. The DFT and MP2 values for the remaining geometrical parameters, in particular those involved in the single HB formed in this dimer, are quite similar (see Fig. 1).

HARMONIC VIBRATIONAL FREQUENCIES

The calculated harmonic vibrational frequencies for hydrogen peroxide and its dimers are summarized in Table II and compared with the MP2-calculated values⁴ and with the experimental ones when available. Table III gives similar results for water and for the hydrogen peroxide-water dimers. Again, for the sake of conciseness, only the results calculated at the 6-311 + G(d,p) are given. The results at the 6-31 + G(d,p) level do not differ greatly from the previous ones and they are not included in the tables. Unfortunately, the experimental vibrational frequencies are only known for

TABLE I.
Rotational Constants (in GHz) for Water Monomer, Hydrogen Peroxide Monomer, Hydrogen Peroxide Dimers, and Water–Hydrogen Peroxide Dimers.

System	6-311 + G(d, p)					
	B-LYP	B-P86	B3-LYP	B3-P86	B3-PW91	MP2
H ₂ O (1)						
A	796.02	793.25	824.36	824.91	824.12	801.58 ^a
B	424.55	426.91	430.02	432.94	432.98	441.83 ^a
C	276.88	277.54	282.60	283.93	283.85	284.83 ^a
H ₂ O ₂ (2)						
A	293.19	294.43	303.35	305.27	305.18	303.01 ^b
B	25.11	25.73	26.46	27.02	26.96	26.73 ^b
C	24.02	24.66	25.35	25.93	25.87	25.59 ^b
(H ₂ O ₂) ₂ (3)						
A	12.43	12.71	13.11	13.38	13.35	13.26 ^b
B	3.59	3.74	3.66	3.80	3.70	3.66 ^b
C	2.83	2.93	2.90	3.00	2.94	2.90 ^b
(H ₂ O ₂) ₂ (4)						
A	15.22	15.47	15.96	16.18	16.31	14.91 ^b
B	2.75	2.89	2.83	2.95	2.85	2.97 ^b
C	2.64	2.77	2.71	2.83	2.74	2.90 ^b
H ₂ O–H ₂ O ₂ (5)						
A	23.71	24.18	25.02	25.44	25.47	25.37 ^c
B	5.54	5.82	5.65	5.91	5.68	5.59 ^c
C	4.58	4.80	4.70	4.90	4.74	4.67 ^c
H ₂ O–H ₂ O ₂ (6)						
A	29.77	31.10	30.49	31.64	32.25	26.16 ^c
B	3.78	3.87	3.93	4.02	3.86	4.42 ^c
C	3.42	3.50	3.55	3.63	3.50	3.85 ^c

^a Values taken from O. Mó, M. Yáñez, and J. Elguero, *J. Chem. Phys.*, **97**, 6628 (1992).

^b Values taken from Ref. 4.

^c Values taken from Ref. 5.

the monomers, for which several sets of values were found in the literature. For the hydrogen peroxide monomer, the two set of values found differ considerably in OH stretching and in torsion frequencies. The MP2 and B-LYP functional calculated results reproduce the OH stretching frequencies fairly well in Chase et al.⁴⁰ (first set), whereas the hybrid functionals yield OH stretching frequencies which clearly agree better with those reported in Redington et al.⁴¹ (second set). Regarding the torsion frequency all methods support the value given in Ref. 40 rather than that of Ref. 41. The remaining frequencies are similarly well reproduced by all the approaches under consideration. It is worth noting, however, that all approaches fail to reproduce the experimental frequency difference between both OH stretching displacements. As shown in Table II all theoretical methods considered in this work predict both

stretchings to be degenerate, whereas they are experimentally predicted to be 9 to 14 cm⁻¹ apart.

For the water monomer, harmonic^{42,43} and anharmonic^{44–46} frequencies have been reported in the literature. The set of harmonic frequencies is quite well reproduced by the three hybrid functionals investigated.

Because the global minimum of the hydrogen peroxide dimers belongs to the C_i symmetry point group, half of its normal vibrational modes, those of a_g symmetry, are ir inactive. Therefore, Table II presents only the frequencies of the nine a_u active modes of species 3. In general, all functionals used, with the exception of the nonhybrid B-LYP approach, slightly overestimate the harmonic frequencies obtained at the MP2 level. It must be taken into account, however, that the MP2 frequencies reported in Refs. 4 and 5 have been scaled by the empirical factor 0.93. The largest

deviations, with regard to the scaled MP2 values, are found when the B3-P86 and B3-PW91 density functionals are used. A similar finding was recently reported for water dimers and water trimers.³⁹

One of the most significant features related to hydrogen bonding is the redshift of the stretching vibration of the proton donor. As shown in Table II, the highest frequencies of the peroxide dimer, **3**, can be assigned to the OH_a and OH_b stretchings. The redshift in OH_a stretching is either zero or negligible, whereas OH_b stretching undergoes a sizeable redshift. At the MP2/6-311 + G(d, p) level this redshift is 114 cm⁻¹, and when the DFT methods are used it becomes significantly larger, ranging from 159 to 199 cm⁻¹. Unfortunately, there are no experimental values for comparison to settle which method yields the most correct description of this physical phenomenon. All approaches predict that the O—O stretching frequencies remain almost unperturbed. The torsion displacement, which should be strongly hindered by the formation of a cyclic dimer, appears blueshifted. In this case, again, the predictions of the MP2 calculations differ from those of the DFT methods. The former yields 267 cm⁻¹ for this frequency shifting, whereas the latter yield values ranging from 310 to 332 cm⁻¹.

The infrared spectrum of **4** is more complex than that of **3** due to the lack of symmetry. The highest vibrational frequency corresponds to the OH_a stretching involving the hydrogen atom bonded to the oxygen, which does not participate in any HB, and, as expected, it appears at the same frequency as in the monomer. The fourth highest frequency band corresponds to the OH_b stretching, and appears redshifted by about 100 cm⁻¹ with respect the monomer at the MP2 level and even to higher frequency values when DFT approaches are used.

It is apparent from Table III that the OH_a stretching of the hydrogen peroxide subunit as well as the O—O stretch remain unperturbed, as far as hydrogen peroxide–water dimer **5** is concerned. In contrast, the OH_b stretch is displaced to low frequencies by 132 cm⁻¹ at the MP2 level, and by higher values (192 to 234 cm⁻¹) at the DFT level. The torsion is blueshifted by about 240 cm⁻¹ at the MP2 level and by about 300 cm⁻¹ when density functionals are used. The strongest discrepancies between MP2 and DFT frequency shiftings are observed for the OH_b stretchings of the water subunit. Whereas the MP2 method predicts

a redshifting of the asymmetric stretch of 100 cm⁻¹, all functionals predict a value five times smaller.

Similar effects are observed for species **6**, although, in this case, they are quantitatively smaller because the interaction between both monomers is also weaker.

BINDING ENERGIES

Regarding the relative stabilities of the different dimers (see Table IV) it can be seen that, at the MP2/6-311 + G(d, p) level,⁴ structure **3** is predicted to be 1.4 kcal/mol more stable than structure **4**. This difference decreases slightly when the basis set is enlarged and it becomes 0.9 kcal/mol when evaluated at the G2(MP2) level. This value is slightly overestimated by all the functionals investigated, which yield values ranging from 1.3 to 1.5 kcal/mol for the **3–4** energy difference when the largest basis set is used. The hydrogen peroxide–water complexes (**5, 6**) correspond to the a/d/ad and 0/a/d sequences. This implies that both oxygen atoms of hydrogen peroxide are involved in hydrogen bonding only in the global minimum. The global minimum, **5**, is found to be 2.4 kcal/mol more stable than the structure **6** at the MP2/6-311 + G(d, p) level,⁵ and 2.2 kcal/mol at the MP2/6-311 + G(3df, 2p) and the G2(MP2) levels of theory. The DFT calculations using the largest basis set give values ranging from 1.7 to 2.2 kcal/mol.

From the values in Table IV it can be also seen that the calculated binding energies after including the ZPE correction decrease as the basis set is enlarged. This finding simply reflects a parallel decrease of the corresponding BSSE, as it is clearly illustrated for the particular case of the B3-P86 functional. It can be noted that the BSSE decreases significantly when increasing the number of polarization functions on both the heavy and the hydrogen atoms, whereas the effect of including diffuse functions on the hydrogen atoms is very small. It must be also observed that the MP2 BSSE corrections are almost twice as large as those found at the DFT level.

Unfortunately, there are no experimental dimerization energies for comparison, so in Table IV we have also given the binding energies obtained at the G2(MP2) level, which can be considered of high accuracy, and can be used as a reliable reference. The general agreement between DFT and G2(MP2) values is reasonably good, even when small basis sets are used, once the BSSE corrections have been included. When G2-type basis sets are employed the largest difference between the

TABLE II.
Harmonic Vibrational Frequencies (cm^{-1}) of the Hydrogen Peroxide Monomer and Hydrogen Peroxide Dimers.

Assignments ^a	6-311 + G(d, p)						Exp ^c
	B-LYP	B-P86	B3-LYP	B3-P86	B3-PW91	MP2 ^b	
H₂O₂ (2)							
Torsion	348	367	368	385	383	367	371, 317
OO stretch	836	873	934	971	965	858	877, 880
OH asym. bend	1226	1242	1298	1314	1315	1213	1266, 1266
OH sym. bend	1383	1394	1453	1465	1465	1357	1402, 1380
OH stretch	3622	3644	3775	3808	3804	3580	3599, 3774
OH stretch	3623	3644	3776	3809	3804	3581	3608, 3788
(H₂O₂)₂ (3)							
Torsion ip	56, 206, 272	58, 226, 298	58, 212, 268	60, 229, 290	60, 213, 279	49, 190, 245	
OO stretch op	677	722	678	717	697	634	
OH _a bend op	832	868	930	967	961	857	
+OH _b bend ip	1268	1283	1338	1354	1355	1251	
OH _a bend op	1433	1454	1500	1518	1511	1392	
+OH _b bend op							
OH _b stretch	3432	3405	3616	3609	3628	3466	
OH _a stretch	3622	3640	3775	3804	3801	3574	
(H₂O₂)₂ (4)							
OH _b bend out-of-plane, torsion op	52, 84, 149, 177	55, 91, 168, 198	46, 87, 152, 182	49, 93, 169, 201	51, 89, 154, 180	45, 84, 123, 169	
Ring def., torsion ip	246, 329	256, 364	257, 324	267, 355	264, 339	236, 288	
OO stretch, OO stretch	545, 587	584, 637	556, 585	589, 626,	573, 592	475, 550	
	832, 843	869, 881	931, 940	967, 978	962, 972	858, 859	
OH _b stretch	1254, 1263	1271, 1282	1323, 1333	1341, 1351	1340, 1350	1231, 1250	
OH _a stretch	1409, 1437	1427, 1454	1476, 1503	1493, 1519	1488, 1513	1373, 1384	
+OH _b stretch op	3442	3414	3622	3617	3638	3471	
OH _a stretch	3492	3464	3666	3662	3683	3500	
+OH _b stretch op							
OH _a stretch op	3622	3640	3775	3804	3802	3571	
+OH _b stretch op							
OH _a stretch	3625	3648	3777	3810	3806	3581	

^a ip and op stand for in-phase and out-of-phase, respectively.

^b MP2 frequencies taken from Ref. 4, and scaled by the empirical factor 0.93.

^c Values taken from Refs. 40 and 41, respectively.

TABLE III.
Harmonic Vibrational Frequencies (cm⁻¹) of Water Monomer and Water – Hydrogen Peroxide Dimers.

Assignments	6-311 + G(d, p)						
	B-P86	B-LYP	B3-LYP	B3-P86	B3-PW91	MP2 ^a	Exp ^b
H ₂ O (1)							
HOH bend	1567	1571	1603	1603	1605	1514	1649 ^c , 1595 ^d , 1589 ^e
OH sym. stretch	3701	3673	3817	3854	3805	3615	3832 ^c , 3652 ^d , 3638 ^e
OH asym. stretch	3809	3778	3922	3962	3958	3756	3942 ^c , 3756 ^d , 3734 ^e
H ₂ O ₂ -H ₂ O (5)							
Intermolecular modes	142, 209, 224	107, 182, 209	119, 186, 217	145, 204, 230	111, 185, 217	101, 171, 197	
Intermolecular modes	281, 338, 519	266, 296, 466	266, 306, 462	280, 336, 504	275, 316, 464	250, 274, 387	
Torsion (H ₂ O ₂)	683	647	655	689	674	610	
OO (H ₂ O ₂) stretch	868	832	929	966	961	858	
	1273, 1479, 1571	1258, 1461, 1574	1329, 1526, 1606	1345, 1543, 1606	1346, 1537, 1609	1242, 1417, 1513	
OH _b (H ₂ O ₂) stretch	3372	3402	3583	3574	3591	3448	
OH _a (H ₂ O ₂) stretch	3617	3628	3776	3786	3805	3582	
OH (H ₂ O) sym. stretch	3647	3631	3781	3811	3809	3587	
OH (H ₂ O) asym. stretch	3775	3756	3900	3931	3932	3620	
H ₂ O ₂ -H ₂ O (6)							
Intermolecular modes	45, 87, 143	43, 80, 140	41, 82, 147	42, 88, 149	46, 83, 141	42, 82, 146	
Intermolecular modes	164, 316, 388	157, 297, 376	164, 300, 397	172, 318, 408	156, 308, 406	164, 246, 396	
OH (H ₂ O ₂) torsion	581	557	563	586	564	521	
OO (H ₂ O ₂) stretch	879	841	939	976	970	861	
	1252, 1393, 1598	1235, 1380, 1600	1306, 1449, 1635	1322, 1463, 1637	1324, 1462, 1637	1217, 1353, 1553	
OH (H ₂ O ₂) stretch	3592	3593	3747	3761	3770	3568	
OH (H ₂ O ₂) stretch	3635	3613	3766	3798	3794	3572	
OH (H ₂ O ₂) sym. stretch	3639	3617	3770	3802	3798	3585	
OH (H ₂ O) asym. stretch	3776	3749	3893	3930	3928	3700	

^a MP2 vibrational frequencies taken from Ref. 5 and scaled by the empirical factor 0.93.
^b The first column corresponds to harmonic frequencies, whereas the remaining ones are anharmonic frequencies.
^c Values taken from Refs. 42 and 43.
^d Values taken from Refs. 44 and 45.
^e Values taken from Ref. 46.

TABLE IV.

Binding Energies (D_0 , in Kilocalories per Mole). Values Within Brackets Are ZPEs Corrections (Kilocalories per Mole). Values Within Parentheses Are FCP Corrected for BSSE.

	B-LYP	B-P86	B3-LYP	B3-P86	B3-PW91	MP2	G2(MP2) ^c	
(H ₂ O ₂) ₂ (3)								
6-31 + G(d, p)	6.0 [33.8]	6.7 [34.2]	6.6 [35.5]	7.2 (5.8) [36.0]	5.8 [35.9]	—		
6-311 + G(d, p)	5.9 [33.8]	6.5 [34.2]	6.5 [35.5]	7.1 (5.7) [35.9]	5.8 [35.8]	7.2 ^a [36.0]		
6-311 + G(3df, 2p)	5.1 (4.5)	5.7 (5.1)	5.6 (5.0)	6.1 (5.4)	4.8 (4.1)	6.9 (5.3)	6.6 (5.0)	6.8 (5.2)
6-311 ++ G(3df, 2p)	5.2 (4.6)	6.0 (5.4)	5.5 (4.9)	6.1 (5.4)	4.7 (4.0)	6.9 (5.3)		
(H ₂ O ₂) ₂ (4)								
6-31 + G(d, p)	4.4 [33.5]	4.8 [33.9]	4.9 [35.1]	5.4 (4.4) [35.6]	4.2 [35.5]	—		
6-311 + G(d, p)	4.3 [33.5]	4.8 [33.9]	4.8 [35.1]	5.3 (4.4) [35.6]	4.2 [35.5]	5.8 ^a [35.4]		
6-311 + G(3df, 2p)	3.6 (3.1)	4.0 (3.4)	4.1 (3.6)	4.5 (3.9)	3.5 (2.9)	5.7 (4.4)	5.5 (4.1)	5.3 (3.9)
6-311 ++ G(3df, 2p)	3.8 (3.2)	4.5 (3.9)	4.1 (3.5)	4.7 (4.1)	3.4 (2.7)	5.7 (4.4)		
H ₂ O ₂ –H ₂ O (5)								
6-31 + G(d, p)	4.5 [31.1]	5.1 [31.4]	5.3 [32.4]	5.6 (4.7) [32.9]	5.0 [32.7]	—		
6-311 + G(d, p)	4.5 [31.0]	4.9 [31.4]	5.1 [32.4]	5.5 (4.6) [32.8]	4.5 [32.6]	5.7 ^b [32.8]		
6-311 + G(3df, 2p)	3.5 (3.1)	3.9 (3.4)	4.0 (3.6)	4.4 (3.9)	3.4 (3.0)	5.1 (4.1)	4.8 (3.9)	4.8 (3.9)
6-311 ++ G(3df, 2p)	3.5 (3.1)	4.1 (3.6)	4.0 (3.6)	4.5 (4.0)	3.4 (2.9)	5.1 (4.1)		
H ₂ O ₂ –H ₂ O (6)								
6-31 + G(d, p)	2.4 [30.4]	2.4 [30.7]	2.7 [31.7]	2.8 (2.2) [32.1]	2.3 [32.0]	—		
6-311 + G(d, p)	2.3 [30.4]	2.4 [30.7]	2.7 [31.7]	2.7 (2.0) [32.1]	2.2 [32.0]	3.3 ^b [32.3]		
6-311 + G(3df, 2p)	1.7 (1.4)	1.7 (1.3)	2.0 (1.6)	2.0 (1.6)	1.5 (1.1)	2.8 (1.9)	2.6 (1.7)	2.8 (1.9)
6-311 ++ G(3df, 2p)	1.8 (1.4)	1.8 (1.4)	2.0 (1.6)	2.2 (1.8)	1.5 (1.1)	2.8 (1.9)		

^a Values taken from Ref. 4.

^b Values taken from Ref. 5.

^c First column corresponds to G2(MP2) energies computed using MP2 / 6-311 + G(d, p)-optimized geometries, whereas the second column was obtained with B3-LYP / 6-311 + G(d, p)-optimized geometries.

G2(MP2) and DFT values is no greater than 0.5 kcal/mol, with the only exceptions being the B-LYP and B3-PW91 approaches, which behave poorly. It can be also noted that the binding energies obtained using the B-P86 and the B3-P86 functionals are systematically closer to the G2(MP2) values than those obtained when the LYP correlation functional is used (B-LYP and B3-LYP, respectively).

We have considered it of interest to check whether a modification of the contributions of the local and nonlocal components of the correlation functional could have a significant effect on the calculated dimerization energies. For this purpose we have chosen, as a suitable case, the B3-LYP functional and we have varied the contributions of the local and the nonlocal correlation functionals by 10% with respect to the standard values.²⁷ Our results show that the calculated binding energies change very little, the largest change being smaller than 0.25 kcal/mol, that is, four times smaller than the change observed on going from the 6-31 + G(d, p) basis set to the 6-311 + G(3df, 2p) basis set.

We have also checked the effect of employing DFT-optimized geometries rather than MP2-optimized ones to get the G2(MP2) energies. For this purpose, we have recalculated the G2(MP2) energies of all systems investigated by using the B3-LYP/6-31 + G(d, p)-optimized geometries and the corresponding ZPE energies rather than the MP2/6-31 + G(d, p) values. The results obtained (see Table IV) differ very little (less than 0.2 kcal/mol) from those obtained when the MP2 geometries and ZPEs are used.

Conclusions

Our study on the performance of different functionals to describe multiple hydrogen bond complexes shows that all investigated functional yield optimized geometries to be in good agreement with the MP2 ones, although the B-LYP approach systematically yields O—O, O···O, and O—H distances that are too large. The largest discrepancies between DFT and MP2 structures, as far as the calculated rotational constants are concerned, are

found for the only dimer which presents a single HB. In general, better agreement with the MP2 values is obtained when the nonlocal hybrid functionals are used.

A redshifting of the OH_b stretching frequencies of the hydrogen peroxide moiety is predicted by all the approaches investigated; however, in all cases, the DFT-estimated shiftings are sizably larger than the corresponding MP2 values. The torsion of the hydrogen peroxide subunit appears blueshifted in the dimers. Again, the DFT values for this shifting are systematically greater than the MP2 ones. The greatest discrepancies between the MP2 and DFT frequency shiftings are observed for the OH_b stretchings of the water subunit of complex 5. Unfortunately, the lack of experimental information does not allow us to conclude which approach is the best suited to reproduce this physical phenomenon.

All functionals reproduce the relative stabilities of the different local minima quite well if the G2(MP2) values are taken as a suitable reference. With the exception of the B-LYP and B3-PW91 approaches, all functionals yield binding energies that differ by less than 0.5 kcal/mol from the G2(MP2) values, provided that G2-type basis sets are used and that the corresponding BSSE corrections are included.

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